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(54) **Process for preparing addition polymerization catalysts via metal center oxidation**
Verfahren zur Herstellung von Additionspolymersiationskatalysatoren via Metalzentraoxidation
Procédé de préparation de catalyseurs pour polymérisation par addition par oxydation de centres
métalliques

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(56) References cited:
EP-A- 0 277 004

• **POLYHEDRON vol. 8, no. 13, 1989, pages 1838 - 1843; BOCHMAN M.: 'Synthesis of cationic alkyl bis(cyclopentadienyl)titanium complexes by one-electron oxidation of titanium(III) alkyls.'**

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0 495 375 B1

Description

This invention relates to a process for preparing certain catalytically active metal complexes. More particularly, this invention relates to such a process involving oxidation of the metal center of a complex to form active catalyst compositions useful for polymerizing olefins, diolefins and/or acetylenically unsaturated monomers.

The use of Ziegler-Natta type catalysts in the polymerization of addition polymerizable monomers is, well known in the prior art. In general, these catalyst systems comprise a Group 4 or Lanthanide metal compound and a metal alkyl cocatalyst, particularly a trialkyl aluminum cocatalyst. Several preparations for homogeneous olefin polymerization catalysts are known. These involve reacting a transition metal chloride with a trialkyl aluminum compound, reacting a transition metal alkyl and a trialkyl aluminum compound, reacting a transition metal alkyl with a proton source, or reacting a transition metal alkyl with a molecular oxidant. In these examples the oxidation state of the transition metal remains unchanged or may actually be reduced.

In Polyhedron, 8(13-14), 1838-1843 (1989), M. Bochmann et al., disclosed an oxidative process for preparing bis (pentamethylcyclopentadienyl)titanium methyl tetraphenylborate using silver tetraphenylborate oxidant in tetrahydrofuran solvent. The complex was inactive in the polymerization of ethylene.

In J. Am. Ch. Soc. 109, 4111-4113 (1987) there is disclosed a process for preparation of cationic zirconium (IV) benzyl complexes by one electron molecular oxidation of d^0 organometallic compounds in tetrahydrofuran or methylene chloride solvent.

In both of the foregoing processes the solvents employed interfered with the resulting complex and detrimentally affected the catalytic ability of the catalyst in subsequent olefin polymerizations. In addition the references employed an oxidizing agent containing tetraphenylborate counter ion. Such anions, it has now been discovered, interfere with the resulting complex and are unacceptable for use in a metal center oxidation process for preparing addition polymerization catalysts.

EP-A-0,277,004 discloses the preparation of a Ziegler-Natta type catalyst by combining a bis(cyclopentadienyl) Group 4 metal (IV) complex with an ion-exchange compound having a cation, which irreversibly reacts with a ligand on the metal complex, and an anion, which is a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom. On combination, the reaction of cation with said ligand generates an ion pair consisting of the Group 4 metal (IV) cation and said anion. The anion can be a borate and exemplified borates include tetrakis(perfluorophenyl)borate.

EP-A-0,416,815 (published March 13, 1991) discloses certain novel constrained geometry complexes possessing unique catalytic properties. EP-A-0,418,044 (published March 20, 1991) discloses certain cationic constrained geometry catalysts that are particularly effective in polymerization of α olefins. EP-A-0,468,651 (published January 29, 1992) discloses a unique oxidative activation procedure for preparing such complexes as are disclosed in EP-A-0,418,044 useful as addition polymerization catalysts.

The present invention lies in the discovery of a novel technique for preparing the foregoing, cationic constrained geometry, metal complexes involving both metal center oxidation and cation complex formation in a single step. By combining what previously required two separate steps utilizing separate reagents and recovery systems, an improved and greatly simplified catalyst preparation is provided.

In accordance with the present invention there is provided a process for the preparation of a catalyst useful for addition polymerizations corresponding to the formula I:



wherein:

L independently each occurrence is an anionic ligand or ligand system;

M is a metal of Group 4-8 of the Periodic Table also having an oxidation state, M^* , one less than the state of the metal in the catalyst;

X independently each occurrence is hydride; halide; or a group selected from alkyl, alkenyl, silyl, germyl, aryl, and combinations thereof having up to 20 carbon, silicon or germanium atoms, and oxygen, halogen, nitrogen, phosphorus and/or sulfur containing derivatives thereof;

ℓ is an integer greater than or equal to 1;

n is an integer greater than or equal to 1, and the sum of ℓ and n together is one less than the valence of M; and

A^- is a monovalent, compatible, noncoordinating anion, corresponding to the formula II:



wherein:

B is boron in a valence state of 3,

X_1 to X_4 are the same or different nonreactive, organyl or silyl radicals containing from 6 to 20 carbon or silicon atoms and optionally two or more of X_1 to X_4 may be linked to each other through a stable bridging group,

the steps of the process comprising contacting, under conditions to form the catalyst, a reduced metal derivative corresponding to the formula III:



wherein:

L , ℓ , n , X , and M^* are as previously defined in connection with formula I with an oxidizing agent capable of oxidizing M^* to form M and which in reduced form is noninterfering with the resulting catalyst, said oxidizing agent corresponding to the formula IV:



wherein:

Ox^+ is a cationic oxidizer capable of oxidizing M^* to form M ; and

A^- is as previously defined in connection with formula I.

All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

The term "anionic ligand or ligand system" refers to any ancillary, electron donating moiety.

Illustrative but nonlimiting examples of suitable anionic ligands include: R , $-R'(OR)_mOR$, $(OR)_mOR$, $-PR_2$, $-SR$, $-OR$, $-NR_2$, hydride, and organometalloid radicals comprising a Group 14 element wherein each of the hydrocarbyl substituents contained in the organic portion of said organometalloid, independently contains from 1 to 20 carbon atoms. In these ligands:

R is a hydrocarbyl, silyl, germlyl or a substituted hydrocarbyl, silyl, or germlyl group of from 1 to 50 carbon, silicon, or germanium atoms;

R' is C_{2-10} alkylene, and

m is an integer from zero to ten.

Preferred anionic ligands are cyclopentadiene; substituted cyclopentadiene; biscyclopentadiene; and bridged biscyclopentadiene groups such as methylene or silane bridged biscyclopentadiene ligands. A most preferred anionic ligand is a substituted cyclopentadiene group more fully described hereafter.

The term "cationic oxidizer" as used herein refers to an organic or inorganic ion having an oxidation potential sufficient to cause oxidation of the Group 4-8 metal center to the next higher oxidation state. Preferred cationic oxidizers have an oxidation potential of at least +0.20 volt and preferably at least +0.25 volt. Examples of suitable cationic oxidizers are ferrocenium, inertly substituted ferrocenium such as C_{1-4} alkyl substituted ferrocenium ions, Ag^+ , triphenylmethyl cation, and azoamines, for example $PhN=N(Ph)_2^+$, wherein Ph is phenyl.

As used herein, the recitation "compatible noncoordinating anion" means an anion which when functioning as a charge balancing anion in the catalyst system of this invention, does not transfer an anionic substituent or fragment thereof to any cationic species thereby forming a neutral metal product. "Compatible anions" are anions which are not degraded to neutrality during catalyst preparation or use. Examples of compatible noncoordinating anions are provided hereafter.

The recitation "metalloid", as used herein, includes nonmetals such as boron, phosphorus which exhibit semi-metallic characteristics.

Preferred metals of Group 4-8 are titanium, zirconium, vanadium, chromium and iron. Especially preferred is titanium, whereby M is Ti(IV) and M* is Ti(III).

In the foregoing catalysts, X may include for example, hydride; halide (especially chloride); primary, secondary or tertiary alkyl; alkoxide; alkoxyalkyl; alkyl(polyalkyleneoxy)alkyl; dialkylaminoalkyl; dialkylaminoaralkyl; allyl; dialkylphosphinoalkyl; and dialkylphosphinoaralkyl. It has been found highly desirable when L is L', as explained hereafter, that X should be capable of stabilizing the resulting complex. In such case X preferably is allyl or amino, phosphino or alkoxy substituted hydrocarbyl of up to 20 carbons.

Preferred reduced metal derivatives for use herein correspond to the formula IIIA:



wherein:

L' is a divalent derivative of a substituted cyclopentadienyl group imparting a constrained geometry to the metal active site and containing up to 50 nonhydrogen atoms;

M* is as previously defined in connection with formula I;

X is a hydrocarbyl or an alkoxy, amino, phosphino or halo substituted hydrocarbyl group of up to 20 carbons; and n is one or two depending on the valence of M*.

By use of the term "constrained geometry" herein is meant that the metal atom is forced to greater exposure of the active metal site because of one or more substituents on the cyclopentadienyl or substituted cyclopentadienyl group forming a portion of a ring structure wherein the metal is both bonded to an adjacent covalent moiety and is held in association with the cyclopentadienyl or substituted cyclopentadienyl group through an η^5 bonding interaction. It is understood that each respective bond between the metal atom and the constituent atoms of the cyclopentadienyl or substituted cyclopentadienyl group need not be equivalent. That is the metal may be symmetrically or unsymmetrically π -bound to the cyclopentadienyl or substituted cyclopentadienyl group.

The geometry of the active metal site is further defined as follows. The center of the cyclopentadienyl or substituted cyclopentadienyl group may be defined as the average of the respective X, Y, and Z coordinates of the atomic centers forming the cyclopentadienyl or substituted cyclopentadienyl group. The angle, θ , formed at the metal center between the center of the cyclopentadienyl or substituted cyclopentadienyl group and each other ligand of the metal complex may be easily calculated by standard techniques of single crystal X-ray diffraction. Each of these angles may increase or decrease depending on the molecular structure of the constrained geometry metal complex. Those complexes wherein one or more of the angles, θ , is less than in a similar, comparative complex differing only in the fact that the constrain-inducing substituent is replaced by hydrogen have constrained geometry for purposes of the present invention. Preferably one or more of the above angles, θ , decrease by at least 5 percent more preferably 7.5 percent compared to the comparative complex. Highly preferably, the average value of all bond angles, θ , is also less than in the comparative complex.

Preferably, monocyclopentadienyl metal coordination complexes according to the present invention have constrained geometry such that the smallest angle, θ , is less than 115° , more preferably less than 110° , most preferably less than 105° .

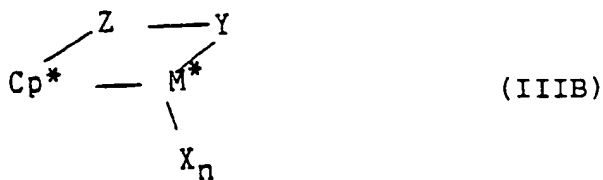
Preferably, L_c in formulae I and III is $-Cp^*-Z-Y$, wherein:

Cp^* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M*;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;

Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system.

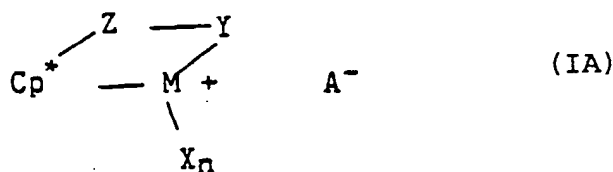
Highly preferred reduced metal derivative compounds are monocyclopentadienyl titanium compounds corresponding to the formula IIIB:



wherein:

M^* , X , and n are as previously defined in connection with formula IIIA;
 Cp^* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M^* ;
 Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements; and
 Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system.

After metal center oxidation the catalysts correspond to the formula IA:

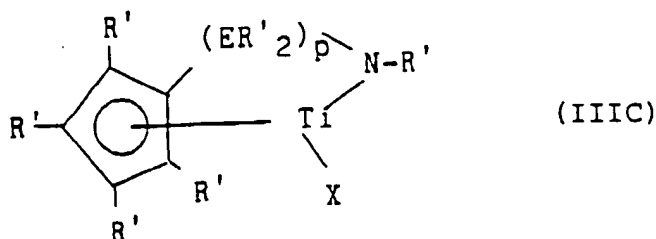


wherein:

Cp^* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M ,
 A^- and M are as defined in connection with formula I, and
 n , X , Y and Z are as previously defined in connection with formula IIIB.

Each of the four remaining carbon atoms in the cyclopentadienyl radical may be substituted or unsubstituted with the same or a different radical selected from hydrocarbyl radicals, substituted-hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from Group 14 of the Periodic Table of the Elements, and halogen radicals. In addition two or more such substituents may together form a fused ring system. Suitable hydrocarbyl and substituted-hydrocarbyl radicals, which may be substituted for at least one hydrogen atom in the cyclopentadienyl radical, will contain from 1 to 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radicals. Suitable organometalloid radicals include mono-, di- and trisubstituted organometalloid radicals of Group 14 elements wherein each of the hydrocarbyl groups contain from 1 to 20 carbon atoms. More particularly, suitable organometalloid radicals include trimethylsilyl, triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl, and trimethylgermyl.

Most highly preferred reduced metal derivatives are amidosilane- or amidoalkanedyl- compounds corresponding to the formula IIIC:



wherein:

R' each occurrence is independently selected from hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X is a hydrocarbyl or an alkoxy, amino, phosphino and/or halo substituted hydrocarbyl group of up to 20 carbons; and

p is 1 or 2.

Examples of the above most highly preferred metal coordination compounds include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, or phenyl; the cyclopentadienyl group is cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, or octahydrofluorenyl; R' on the foregoing cyclopentadienyl groups each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, or phenyl; and X is methyl, ethyl, allyl, neopentyl, trimethylsilyl, norbornyl, benzyl, methylbenzyl, (dimethylamino)benzyl, (dimethylphosphino)benzyl, (diperfluorophenylamino)-benzyl, or phenyl.

Specific preferred reduced metal compounds include: (tert-butylamido) (tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylamino)benzyl, (tert-butylamido) (tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylamino)benzyl, (methylamido) (tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium allyl, (methylamido) (tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylphosphino)benzyl, (ethylamido) (tetramethyl- η^5 -cyclopentadienyl)-methylene titanium 2-(diperfluorophenylamino)benzyl, (tert-butylamido)dibenzyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium 2-(dimethylamino)benzyl, (benzylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium (dimethylaminomethyl)dimethylsilyl, and (phenylphosphido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium 2-(dimethylamino)benzyl.

In the most preferred embodiment -Z-Y- is an amidosilane or amidoalkane group of up to 10 nonhydrogen atoms, for example (tert-butylamido) (dimethylsilyl) and (tert-butylamido)-1-ethane-2-yl.

Other reduced metal derivatives which are useful in the process of this invention, especially compounds containing other Group 4-8 metals will be apparent to those skilled in the art.

Compounds useful as oxidizing agents in the preparation of the compounds of this invention preferably comprise a cationic oxidizer, and one or more compatible noncoordinating anions, as previously explained.

A⁺ of formula I is represented by formula II:



wherein:

B is boron in a valence state of 3;

X₁ to X₄ are the same or different nonreactive, organyl or silyl radicals containing from 6 to 20 carbon or silicon atoms. In addition two or more of X₁ to X₄ may be linked to each other through a stable bridging group. Preferably X₁ to X₄ lack reactive hydrogen moieties. That is, the radicals are either devoid of hydrogen, contain only hydrogen in nonactivated positions or contain sufficient steric hindrance to protect potentially active hydrogen sites. Examples of preferred radicals for X₁ to X₄ are perfluorinated hydrocarbyl radicals containing from 1 to 20 carbon atoms, 3,4,5-trifluorophenyl, and 3,5-di(trifluoromethyl)phenyl. One of X₁ to X₄ may be a C₁₋₁₀ organyl group, especially methyl or benzyl, without detrimentally affecting the inert properties of the anion.

A most highly preferred compatible, noncoordinating, anion is tetra(pentafluorophenyl)borate.

Suitable organic cationic oxidizers for use according to the present invention include ferrocenium ions, bis-indenyl Fe(III) ions, and cationic derivatives of substituted ferrocene, molecules, especially methyl substituted ferrocene. Suitable metal cationic oxidizers include Ag⁺, Pd⁺, Pt⁺, Hg⁺, Hg₂⁺, Au⁺ and Cu⁺. Most preferred cationic oxidizers are ferrocenium, substituted ferrocenium, and Ag⁺ cations.

Illustrative, but not limiting, examples of oxidizing agents in the preparation of the improved catalysts of this invention are ferrocenium tetra(pentafluorophenyl)borate, 1,1'-dimethylferrocenium tetrakis(perfluorophenyl) borate, gold (I) tetrakis 3,4,5-trifluorophenyl borate, silver tetra(pentafluorophenyl)borate, and 1,1'-dimethylferrocenium tetrakis 3,5-bistrifluoromethylphenyl borate.

To recapitulate, it should be noted that the two compounds combined for preparation of the active catalyst must be selected so as to avoid transfer of a fragment of the anion, particularly an aryl group, to the metal cation, thereby forming a catalytically inactive species. This may be done by providing sufficient steric hindrance resulting from substituents on the groups attached to the Group 4-8 reduced metal derivative as well as substituents on the aromatic carbon atoms of the anion. It follows, then, that Group 4-8 reduced metal derivatives comprising perhydrocarbyl-sub-

stituted cyclopentadienyl radicals, for example, could be effectively used with a broader range of oxidizing agents than could reduced metal compounds comprising less bulky radicals. As the amount and size of the metal substituents are reduced, however, more effective catalysts are obtained with oxidizing agents containing anions which are more resistant to degradation, such as those with substituents on the meta and/or para positions of the phenyl rings. Another means of rendering the anion more resistant to degradation is afforded by fluorine substitution, especially perfluoro-substitution, in the anion. Oxidizing agents containing fluoro-substituted stabilizing anions may, then, be used with a broader range of first components. A preferred stabilizing anion is tetrakisperfluorophenylborate.

In general, the catalyst can be prepared by combining the reduced metal derivative and oxidizing agent in a suitable noninterfering, noncoordinating solvent at a temperature from -100°C to 300°C, and recovering the resulting product.

"Addition polymerizable monomers" usefully polymerized by catalysts prepared according to the process of the present invention include for example ethylenically unsaturated monomers, acetylenic compounds, conjugated or non-conjugated dienes, polyenes, and carbon monoxide. Preferred monomers include the C₂₋₁₀ α -olefins especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, C₁₋₄ alkyl substituted styrene, tetrafluoroethylene, vinylbenzocyclobutane, ethyridenenorbornene and 1,4-hexadiene.

In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, for example, temperatures from 0 -250°C and pressures from atmospheric to 1000 atmospheres (0.1 to 100 MPa). Suspension, solution, slurry or gas phase process condition may be employed. A support may be employed but preferably the catalysts are used in a homogeneous manner. Hydrogen or similar chain terminator may be employed to control polymer molecular weight. It will, of course, be appreciated that the catalyst system will form in situ if the components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

Suitable solvents for the formation of the catalyst are noncoordinating, inert liquids. Examples include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated hydrocarbons such as perfluorinated C₄₋₁₀ alkanes, and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, divinylbenzene, allylbenzene, and vinyltoluene (including all isomers alone or in admixture). Mixtures of the foregoing are also suitable.

It is believed that the active catalyst species of the present invention contains a metal center which remains cationic and has a metal-carbon bond which is reactive with olefins, diolefins and acetylenically unsaturated compounds. Also associated with this metal center are the charge balancing anionic remnant of the formula A⁻.

The catalyst formed by the method of this invention may be retained in solution or separated from the solvent, isolated, and stored for subsequent use. As previously indicated supra, the catalyst may also be prepared in situ during a polymerization reaction by passing the separate components into the polymerization vessel where the components will contact and react to produce the improved catalyst of this invention.

The equivalent ratio of reduced metal derivative to oxidizing agent employed in the process is preferably in a range from 0.1:1 to 10:1, more preferably from 0.75:1 to 2:1, most preferably 1.0:1.0. In most polymerization reactions the equivalent ratio of catalyst:polymerizable compound employed is from 10⁻¹²:1 to 10⁻¹:1, more preferably from 10⁻⁸:1 to 10⁻⁵:1.

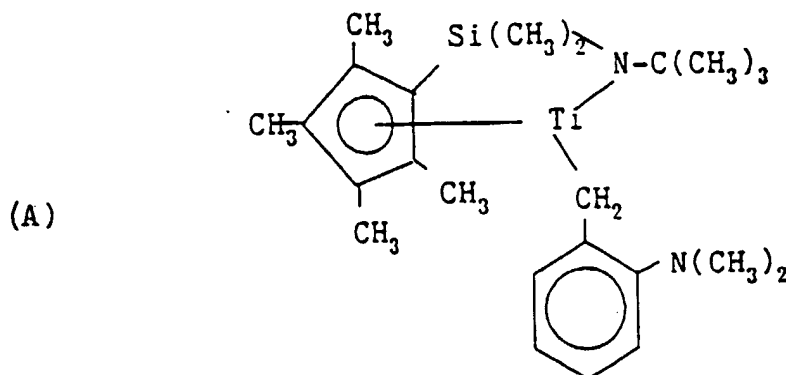
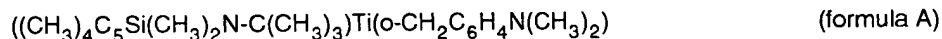
A beneficial feature of some of the catalysts of this invention, particularly those based on monocyclopentadienyl substituted titanium compounds in combination with an oxidizing agent comprising boron, is that when the catalysts of this invention are used to copolymerize α -olefins, either alone or in combination with diolefins, the amount of higher molecular weight olefin or diolefin incorporated into the copolymer is significantly increased when compared to copolymers prepared with the more conventional Ziegler-Natta type catalysts. The relative rates of reaction of ethylene and higher α -olefins with the aforementioned titanium-based catalysts of this invention are so similar that the monomer distribution in copolymers prepared with the catalysts of this invention may be controlled by the ratio of monomeric reactants. Certain of the catalysts are also useful to prepare polymers of vinylaromatic monomers having a high degree of syndiotacticity. Such catalysts have been disclosed in EP-A-0421659 (published April 10, 1991).

In general, catalysts prepared by the present process produce polymer products which will be free of certain trace impurities generally found in polymers produced with Ziegler-Natta type catalysts such as aluminum, magnesium, and chloride. The polymer products produced with the catalysts of this invention should, then, have a broader range of applications than polymers produced with more conventional Ziegler-Natta type catalysts comprising a metal alkyl such as an aluminum alkyl.

Having described the invention the following examples are provided as further illustration thereof and are not to be construed as limiting. Unless stated to the contrary all parts and percentages are expressed on a weight basis.

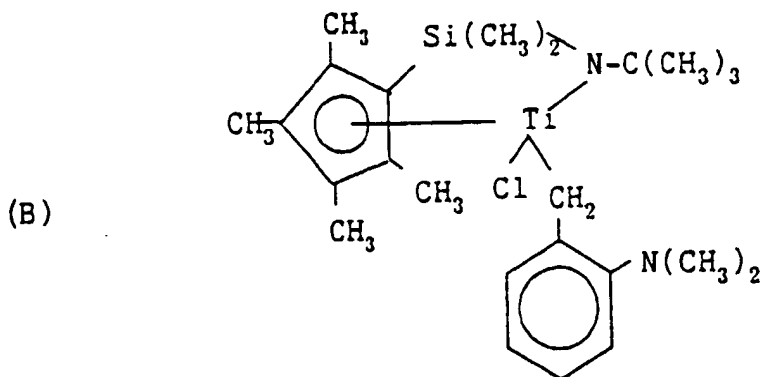
Example 1

(A) Preparation of reduced metal derivative (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)-silanetitanium (III) (orthodimethylamino) benzyl,

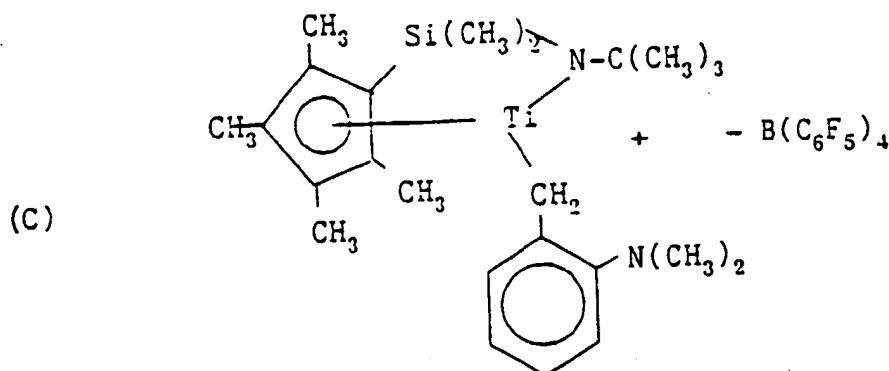
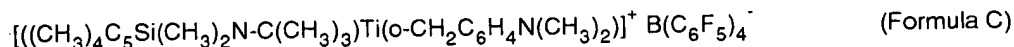


In the drybox were placed 0.25 g of $TiCl_3(THF)_3$ and 0.35 g of $(MgCl)_2((CH_3)_4C_5Si(CH_3)_2N-C(CH_3)_3)(THF)_2$, prepared according to the technique of EP-A-0,416,815 by reaction of (tert-butylamido)dimethyl(tetramethylcyclopentadienyl)silane with isopropylmagnesium chloride in a molar ratio of 1:2. The silane starting reactant was prepared by reacting dimethyldichloro silane with sodium 1,2,3,4-tetramethylcyclopentadienide at $-40^\circ C$ in tetrahydrofuran solvent, followed by reaction of the recovered product with butylamine in tetrahydrofuran at $25^\circ C$ for several hours were mixed at $25^\circ C$. 15 mL of tetrahydrofuran (THF) were added to give a purple solution. After 5 minutes, 95 mg of (o-dimethylamino)benzyl lithium, $o-LiCH_2C_6H_4N(CH_3)_2$, prepared by reaction of n-butyl lithium with o-(dimethylamino)toluene in refluxing tetrahydrofuran in 5 mL of THF were added. After 30 minutes, the volatile materials were removed under reduced pressure to yield a red-brown solid. Pentane (20 mL) was added, the solution was filtered, and the volatile materials were removed to give a sticky red-brown solid. This solid was again dissolved in pentane, filtered, and cooled to $-45^\circ C$. Red crystals were isolated by filtration and dried. The electron paramagnetic resonance (EPR) spectrum of this material exhibited a single line at room temperature ($g=1.974$) and 2 lines at 77 K (consistent with a plane of symmetry in the molecule).

Proper identity of the reduced metal complex was confirmed by also preparing the $Ti(IV)$ chloride of the above complex (Formula B) by reaction with lead (II) chloride and analyzing the NMR spectra.



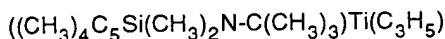
(B) Preparation of catalyst: (tert-butylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silanetitanium (IV) o-dimethylaminobenzyl tetrakis(perfluorophenyl)borate



A 50 ml flask was charged with 0.170 g of $((CH_3)_4C_5Si(CH_3)_2N-C(CH_3)_3)Ti(o-CH_2C_6H_4N(CH_3)_2)$ (0.463 mmol) and 25 ml of toluene. To the resulting red solution 0.280 g (0.382 mmol) of ferrocenium tetrakis-perfluorophenyl borate was added as a solid. The solution was stirred for one hour. After this time period the solvent was removed under reduced pressure to give a red oil. The resulting oil was triturated with pentane to give an orange solid. The solid was collected by filtration and washed with toluene (150 ml), dried under reduced pressure to give 0.289 g (69 percent yield) of product. 1H NMR (thf- d_8) δ 7.57-7.65 (m, 4H), 2.71 (s, 3H), 2.33 (bs, 3H), 2.21 (s, 3H), 0.84 (s, 9H), 0.71 (s, 6H).

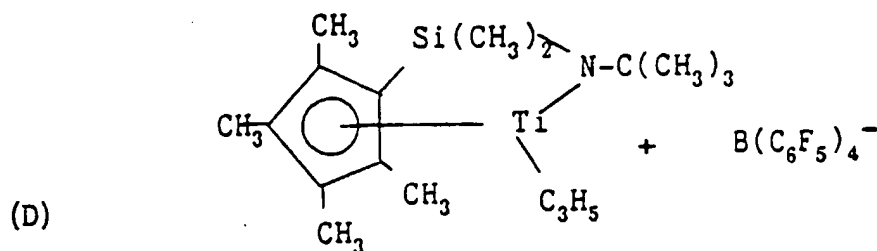
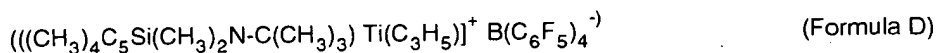
Example 2

(A) Preparation of reduced metal derivative (tert-butylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)silane titanium (III) allyl,



In the drybox, 0.30 g of $TiCl_3(THF)_3$ and 0.42 g of $(MgCl)_2((CH_3)_4C_5Si(CH_3)_2N-C(CH_3)_3)(THF)_2$ were mixed in a Schlenk tube. 20 mL of THF was added to give a purple solution. The Schlenk tube was sealed and removed to a Schlenk line, and the solution was cooled to -30°C. 0.81 mL of 1.0 M allylmagnesium bromide was added by syringe. After 20 minutes, the solution was warmed to 0°C and the volatile materials were removed under reduced pressure to yield a dark solid. While keeping the flask at 0°C pentane (30 mL) was added, and the deep red solution was filtered, concentrated to ca. 5-7 mL, and cooled to -40°C. Red crystals were isolated by filtration and dried in 22 percent yield. The EPR spectrum of this material exhibited a single line at room temperature and 2 lines at 77 K (consistent with a plane of symmetry in the molecule).

(B) Preparation of catalyst: (tert-butylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)silane titanium (IV) allyl tetrakis(pentafluorophenyl)borate



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The reaction conditions of Example 1 were substantially repeated using equal molar amounts of the above reduced metal derivative and ferrocenium tetrakis-perfluorophenyl borate as the anionic oxidizer to cause metal center oxidation.

Polymerizations

A 2 L stirred reactor was charged with the desired amounts of mixed alkane solvent (Isopar™ E, available from Exxon Inc.) and 1-octene comonomer. The reactor was heated to the polymerization temperature and saturated with ethylene at the desired pressure. Hydrogen chain terminator was added by differential pressure expansion from a 75 mL addition tank. Catalyst was prepared in a drybox by syringing the desired amount of 0.0050 M reduced metal derivative solution (in toluene) into a suspension of the solid cationic oxidizer in toluene to provide equal molar ratios of reduced metal derivative and cationic oxidizer. This solution was then transferred to a catalyst addition tank and injected into the reactor. The polymerization was allowed to proceed for the desired time and the solution was removed from the reactor and quenched with hindered phenol anti-oxidant and isopropanol. The polymers were air-dried overnight and then dried in a vacuum oven.

A comparative example was provided utilizing the reduced metal derivative of Examples 1 but using a cationic oxidizer having a coordinating or interfering anion, tetraphenylborate. The comparative polymerization resulted in drastically reduced reaction yield.

Results are contained in Table I.

Table I

Run	Catalyst	Cat. Amt. μmole	Solvent (ml)	Comonomer (ml)	Ethylene KPa	ΔH_2 KPa	Temp. $^{\circ}\text{C}$	Time (Min.)	Polymer (g)
1	Ex. 1	10	1000	200	3100	340	130	10	192.0
2	Ex. 1	2.5	1150	50	3400	70	150	10	57.8
3	Ex. 1	1	1100	100	3400	70	150	10	55.3
4	Ex. 2	10	1000	200	3100	340	130	10	73.5
5	Ex. 2	10	850	350	3100	170	90	15	228.4
*	1.	10	1000	200	3400	340	130	15	69.7

* comparative
 1. $(\text{Me}_4\text{C}_5\text{SiMe}_2\text{N-tert-Bu})\text{Ti}(\text{o-CH}_2\text{C}_6\text{H}_4\text{NMe}_2)$ and $[(\text{MeC}_5\text{H}_4)_2\text{Fe}]^+ [\text{Ph}_4\text{B}]^-$

Claims

1. A process for the preparation of a catalyst useful for addition polymerizations corresponding to the formula I:



wherein:

L independently each occurrence is an anionic ligand or ligand system;
 M is a metal of Group 4-8 of the Periodic Table also having an oxidation state, M^* , one less than the state of the metal in the catalyst;
 X independently each occurrence is hydride; halide; or a group selected from alkyl, alkenyl, silyl, germyl, aryl, and combinations thereof having up to 20 carbon, silicon or germanium atoms, and oxygen, halogen, nitrogen, phosphorus and/or sulfur containing derivatives thereof;
 ℓ is an integer greater than or equal to 1;
 n is an integer greater than or equal to 1, and the sum of ℓ and n together is one less than the valence of M; and
 A^- is a monovalent, compatible, noncoordinating anion corresponding to the formula II:



wherein:

B is boron in a valence state of 3,
 X_1 to X_4 are the same or different nonreactive, organyl or silyl radicals containing from 6 to 20 carbon or silicon atoms and optionally two or more of X_1 to X_4 may be linked to each other through a stable bridging group,

the steps of the process comprising contacting, under conditions to form the catalyst, a reduced metal derivative corresponding to the formula III:



wherein:

L , ℓ , n, X, and M^* are as previously defined in connection with formula I
 with an oxidizing agent capable of oxidizing M^* to form M and which in reduced form is noninterfering with the resulting catalyst, said oxidizing agent corresponding to the formula IV.



wherein:

Ox^+ is a cationic oxidizer capable of oxidizing M^* to form M; and
 A^- is as defined above in connection with formula I.

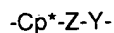
2. A process according to Claim 1, wherein L is an anionic ligand selected from R, $-R'(OR')_mOR$, $(OR')_mOR$, $-PR_2$, $-SR$, $-OR$, $-NR_2$, hydride, and organometalloid radicals comprising a Group 14 element wherein each of the hydrocarbyl substituents contained in the organic portion of said organometalloid, independently, contains from 1 to 20 carbon atoms, wherein

R is a hydrocarbyl, silyl, germyl or a substituted hydrocarbyl, silyl, or germyl group of from 1 to 50 carbon, silicon, or germanium atoms;

R' is C_{2-10} alkylene, and

m is an integer from zero to ten.

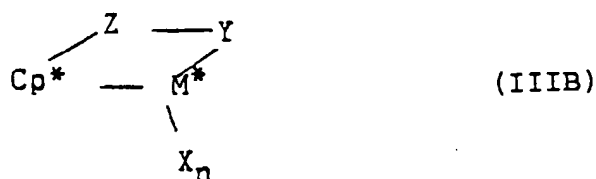
3. A process according to Claim 1, wherein L_{ℓ} is



wherein:

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M*;
 Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;
 Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system.

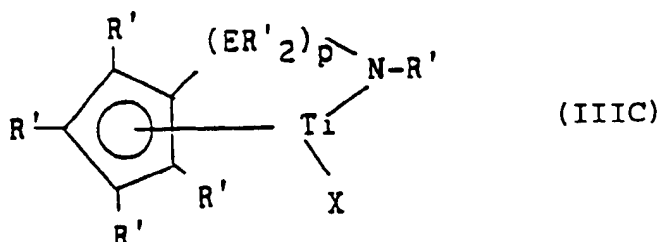
4. A process according to Claim 3, wherein $\text{L}_\ell \text{M}^* \text{X}_n$ corresponds to the formula III B:



wherein:

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M*;
 M* is a metal of Group 4-8 of the Periodic Table in an oxidation state one less than the state of the metal (M) in the product of formula I;
 n is one or two depending on the valence of M*;
 X is a hydrocarbyl or an alkoxy, amino, phosphino and/or halo substituted hydrocarbyl group of up to 20 carbons;
 Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;
 and
 Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system.

5. A process according to any one of the preceding claims, wherein said oxidizing agent has an oxidation potential of at least +0.20 volt.
6. A process according to any one of the preceding claims, wherein X_1 , X_2 , X_3 , and X_4 are perfluorinated hydrocarbyl radicals containing from 1 to 20 carbons.
7. A process according to Claim 6, wherein said anion is tetra(pentafluorophenyl)borate.
8. A process according to any one of the preceding claims, wherein Ox^{+a} is ferrocenium, inertly substituted ferrocenium, or Ag^{+1} .
9. A process according to any one of the preceding claims, wherein M is titanium.
10. A process according to Claim 4, wherein $\text{L}_\ell \text{M}^* \text{X}_n$ corresponds to the formula III C:



wherein:

R' each occurrence is independently selected from hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X is a hydrocarbyl or an alkoxy, amino, phosphino and/or halo substituted hydrocarbyl group of up to 20 carbons; and

p is 1 or 2.

11. A process according to Claim 10, wherein R' on the amido group is butyl.

12. A process according to Claim 10, wherein E is silicon.

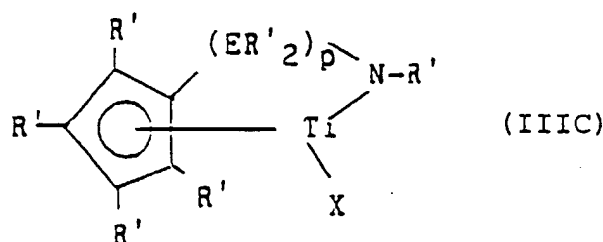
13. A process according to Claim 10, wherein X is methyl or benzyl.

14. A process according to Claim 4, wherein -Z-Y- is (tert-butylamido) dimethylsilyl.

15. A process according to any one of the preceding claims, wherein the process is conducted in situ during an addition polymerization reaction by passing said reduced metal reaction derivative and oxidizing agent into the polymerization vessel.

16. A process according to any one of the preceding claims, additionally comprising supporting the catalyst on a support.

17. A compound of the formula IIIC:



wherein:

R' each occurrence is independently selected from hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X is a hydrocarbyl or an alkoxy, amino, phosphino and/or halo substituted hydrocarbyl group of up to 20 carbons; and

p is 1 or 2.

18. A compound according to Claim 17, wherein R' on the amido group is butyl.

19. A compound according to Claim 17, wherein E is silicon.

20. A compound according to Claim 17, wherein X is methyl or benzyl.

21. A compound according to Claim 17, selected from (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium (III) (orthodimethylamino)benzyl and (tert-butylamido) dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium (III) allyl.

Patentansprüche

1. Verfahren zur Herstellung eines Katalysators für Additionspolymerisationen, welcher der Formel I entspricht:



in der:

L unabhängig voneinander bei jedem Auftreten ein anionischer Ligand oder ein anionisches Ligandensystem ist,

M ein Metall aus den Gruppen 4-8 des Periodensystems ist, welches auch einen Oxidationszustand M^* hat mit einer um eins kleineren Oxidationsstufe als das Metall in dem Katalysator,

X unabhängig voneinander bei jedem Auftreten Hydrid, Halogenid oder eine Gruppe, ausgewählt aus Alkyl, Alkenyl, Silyl, Germyl, Aryl und Kombinationen daraus mit bis zu 20 Kohlenstoff-, Silicium- oder Germaniumatomen und sauerstoff-, halogen-, stickstoff-, phosphor- und/oder schwefelhaltigen Derivaten dergleichen,

ℓ eine ganze Zahl größer oder gleich 1 ist,

n eine ganze Zahl größer oder gleich 1 ist und die Summe von ℓ und n eins weniger als die Valenz von M beträgt, und

A^- ein monovalentes, kompatibles, nichtkoordinierendes Anion entsprechend der Formel II ist:



in der:

B Bor im Valenzzustand 3 ist,

X_1 bis X_4 die gleichen oder unterschiedliche nichtreaktive Organyl- oder Silylreste mit 6 bis 20 Kohlenstoff- oder Siliciumatomen sind und wahlweise zwei oder mehr der X_1 bis X_4 miteinander über eine stabile, verbindende Gruppe verbunden sein können,

wobei das Verfahren umfaßt: Inkontaktbringen eines reduzierten Metallderivats entsprechend der Formel III



in der:

L, ℓ , n, X und M^* wie zuvor in Formel (I) definiert sind, unter Bedingungen zur Bildung eines Katalysators mit einem oxidierenden Mittel, das fähig ist, M^* unter Bildung von M zu oxidieren und welches in reduzierter Form den resultierenden Katalysator nicht beeinflußt, wobei das oxidierende Mittel der Formel IV entspricht:



in der:

Ox^+ ein kationisches Oxidationsmittel ist, das fähig ist,

M^* unter Bildung von M zu oxidieren, und

A^- wie oben in Formel I definiert ist.

2. Verfahren nach Anspruch 1, in dem L ein anionischer Ligand, ausgewählt aus R, $-R'(OR')_mOR$, $(OR')_mOR$, $-PR_2$, $-SR$, $-OR$, $-NR_2$, Hydrid und Organometalloidresten ist, die ein Gruppe 14 Element enthalten und wobei jeder Kohlenwasserstoffsubstituent, der in dem organischen Teil dieser Organometalloide enthalten ist, unabhängig 1 bis 20 Kohlenstoffatome enthält, wobei

R eine Kohlenwasserstoff-, Silyl-, Germyl- oder eine substituierte Kohlenwasserstoff-, Silyl- oder Germylgruppe mit 1 bis 50 Kohlenstoff-, Silicium- oder Germaniumatomen ist,

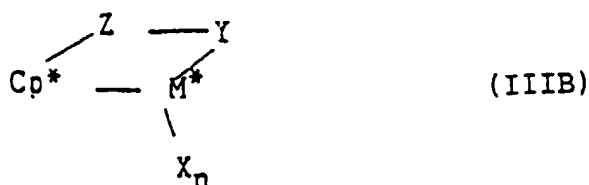
R' C_{2-10} -Alkylen ist und

m eine ganze Zahl von null bis zehn ist.

3. Verfahren nach Anspruch 1, in dem L_ℓ -Cp*-Z-Y- ist, wobei

- 5 Cp* eine Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe ist, die über eine η^5 -Bindung an M* gebunden ist,
 Z eine divalente Einheit ist, die Sauerstoff, Bor oder ein Mitglied der Gruppe 14 des Periodensystems der Elemente enthält,
 Y eine verbindende Gruppe ist, die Stickstoff, Phosphor, Sauerstoff oder Schwefel enthält, und Z und Y zu-
 10 sammen wahlweise ein kondensiertes Ringsystem bilden.

4. Verfahren nach Anspruch 3, in dem L_ℓ M*X_n der Formel III B entspricht:



in der:

- 25 Cp* eine Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe ist, die über eine η^5 -Bindung an M* gebunden ist,
 M* ein Metall aus den Gruppen 4-8 des Periodensystems ist in einem Oxidationszustand mit einer um eins kleineren Oxidationsstufe als der Zustand des Metalls (M) im Produkt der Formel I,
 n eins oder zwei ist in Abhängigkeit der Valenz von M*,
 30 X eine Kohlenwasserstoff- oder eine alkoxy-, amino-, phosphino- und/oder halogensubstituierte Kohlenwasserstoffgruppe mit bis zu 20 Kohlenstoffen ist,
 Z eine divalente Einheit ist, die Sauerstoff, Bor oder ein Mitglied der Gruppe 14 des Periodensystems der Elemente enthält, und
 Y eine verbindende Gruppe ist, die Stickstoff, Phosphor, Sauerstoff oder Schwefel enthält, und wahlweise Z
 35 und Y zusammen ein kondensiertes Ringsystem bilden.

5. Verfahren nach einem der vorstehenden Ansprüche, in dem das oxidierende Mittel ein Oxidationspotential von mindestens +0,20 V hat.

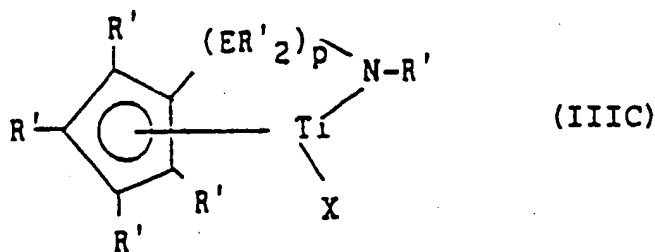
40 6. Verfahren nach einem der vorstehenden Ansprüche, in dem X₁, X₂, X₃ und X₄ perfluorierte Kohlenwasserstoffreste mit 1 bis 20 Kohlenstoffen sind.

7. Verfahren nach Anspruch 6, in dem das Anion Tetra(pentafluorphenyl)borat ist.

45 8. Verfahren nach einem der vorstehenden Ansprüche, in dem Ox^{+a} Ferrocenium, inert substituiertes Ferrocenium oder Ag⁺¹ ist.

9. Verfahren nach einem der vorstehenden Ansprüche, in dem M Titan ist.

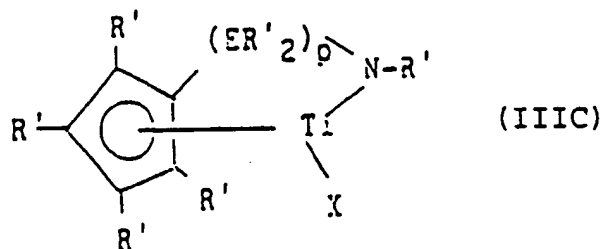
50 10. Verfahren nach Anspruch 4, in dem L_ℓ M*X_n der Formel IIIC entspricht:



in der:

R' bei jedem Auftreten unabhängig ausgewählt ist aus Wasserstoff, Silyl, Alkyl, Aryl und Kombinationen davon mit bis zu 10 Kohlenstoff- oder Siliciumatomen,
 E Silicium oder Kohlenstoff ist,
 X eine Kohlenwasserstoff- oder eine alkoxy-, amino-, phosphino- und/oder halogensubstituierte Kohlenwasserstoffgruppe mit bis zu 20 Kohlenstoffatomen ist und
 p 1 oder 2 ist.

11. Verfahren nach Anspruch 10, in dem R' an der Amidogruppe Butyl ist.
12. Verfahren nach Anspruch 10, in dem E Silicium ist.
13. Verfahren nach Anspruch 10, in dem X Methyl oder Benzyl ist.
14. Verfahren nach Anspruch 4, in dem -Z-Y- (tert-Butylamido)dimethylsilyl ist.
15. Verfahren nach einem der vorstehenden Ansprüche, in dem das Verfahren in situ während der Additionspolymerisation durch Überführen des Metallreaktionsderivats und des oxidierenden Mittels in das Polymerisationsgefäß durchgeführt wird.
16. Verfahren nach einem der vorstehenden Ansprüche, welches zusätzlich das Aufbringen des Katalysators auf einen Träger umfaßt.
17. Verbindung der Formel IIIIC



in der:

R' bei jedem Auftreten unabhängig ausgewählt ist aus Wasserstoff, Silyl, Alkyl, Aryl und Kombinationen davon mit bis zu 10 Kohlenstoff- oder Siliciumatomen,
 E Silicium oder Kohlenstoff ist,
 X eine Kohlenwasserstoff- oder eine alkoxy-, amino-, phosphino- und/oder halogensubstituierte Kohlenwasserstoffgruppe mit bis zu 20 Kohlenstoffatomen ist und
 p 1 oder 2 ist.

18. Verbindung nach Anspruch 17, in der R' an der Amidogruppe Butyl ist.

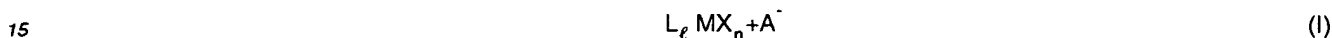
19. Verbindung nach Anspruch 17, in der E Silicium ist.

20. Verbindung nach Anspruch 17, in der X Methyl oder Benzyl ist.

5 21. Verbindung nach Anspruch 17, ausgewählt aus (tert-Butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silan-titan-(III)(orthodimethylamino)benzyl und (tert-Butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silantitan(III) allyl.

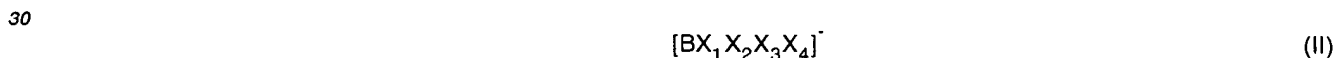
10 Revendications

1. Procédé pour la préparation d'un catalyseur utile pour les polymérisations par addition correspondant à la formule I:



dans laquelle:

20 L indépendamment dans chaque cas est un ligand anionique ou un système de ligand;
 M est un métal du groupe 4-8 du tableau périodique des éléments possédant également un degré d'oxydation, M^* , inférieur d'une unité à l'état du métal dans le catalyseur;
 X indépendamment dans chaque cas est un hydruure, un halogénure, ou un groupe choisi parmi les groupes alkyle, alcényle, silyle, germyle, aryle et leurs combinaisons ayant jusqu'à 20 atomes de carbone, de silicium
 25 ou de germanium, et leurs dérivés contenant de l'oxygène, un halogène, de l'azote, du phosphore et/ou du soufre;
 ℓ est un nombre entier supérieur ou égal à 1;
 n est un nombre entier supérieur ou égal à 1, et la somme de ℓ et n est inférieure d'une unité à la valence de M; et
 A^{-} est un anion monovalent, compatible, de non-coordination correspondant à la formule (II):



dans laquelle:

35 B est un atome de bore de valence 3,
 X_1 à X_4 sont des radicaux organyle ou silyle non-réactifs identiques ou différents, contenant de 6 à 20 atomes de carbone ou de silicium, et éventuellement deux ou plusieurs de X_1 à X_4 peuvent être reliés entre eux par l'intermédiaire d'un groupe de pontage stable,

40 les étapes du procédé comprenant la mise en contact, dans des conditions pour former le catalyseur, d'un dérivé métallique réduit correspondant à la formule (III):



dans laquelle:

L, ℓ , n, X et M^* sont tels que décrits précédemment en relation avec la formule I
 avec un agent d'oxydation capable d'oxyder M^* pour former M et qui sous la forme réduite n'interfère pas avec le
 50 catalyseur obtenu, ledit agent d'oxydation correspondant à la formule IV:



dans laquelle:

Ox^{+} est un oxydant cationique capable d'oxyder M^* pour former M; et
 A^{-} est tel que défini précédemment en relation avec la formule I.

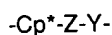
2. Procédé selon la revendication 1, dans lequel L est un ligand organique choisi parmi R, $-R'(OR')_mOR$, $(OR')_mOR$, $-PR_2$, $-SR$, $-OR$, $-NR_2$, un hydruure, les radicaux organométalloïdes comprenant un élément du groupe 14 dans lequel chacun des substituants hydrocarbyle contenus dans la portion organique dudit organométalloïde, contient de 1 à 20 atomes de carbone,

R étant un groupe hydrocarbyle, silyle, germyle ou hydrocarbyle silyle ou germyle substitué, de 1 à 50 atomes de carbone, de silicium ou de germanium;

R' est un groupe alcylène en C_1 à C_{10} , et

m est un nombre entier de 0 à 10.

3. Procédé selon la revendication 1, dans lequel L_f est:



Cp^* est un groupe cyclopentadiényle ou cyclopentadiényle substitué lié à M^* dans un mode de liaison η^5 ;
Z est un groupe divalent comprenant de l'oxygène, du bore, ou un élément du groupe 14 du tableau périodique des éléments;

Y est un groupe de liaison comprenant de l'azote, du phosphore, de l'oxygène ou du soufre, ou éventuellement Z et Y forment ensemble un système de cycles condensés.

4. Procédé selon la revendication 3, dans lequel $L_f M^* X_n$ correspond à la formule IIIB



dans laquelle:

Cp^* est un groupe cyclopentadiényle ou cyclopentadiényle substitué lié dans un mode de liaison η^5 à M^* ;

M^* est un métal du groupe 4-8 du tableau périodique des éléments dans un degré d'oxydation inférieur d'une unité à celui du métal (M) dans le produit de la formule I;

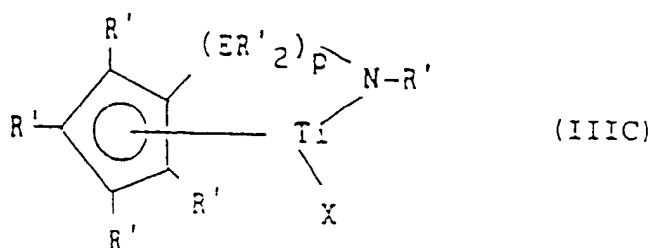
n vaut un ou deux en fonction de la valence de M^* ;

X est un groupe hydrocarbyle ou un groupe hydrocarbyle substitué par un groupe alcoxy, amino, phosphino ou halogéno ayant jusqu'à 20 atomes de carbone;

Z est un groupe divalent comprenant de l'oxygène, du bore, ou un élément du groupe 14 du tableau périodique des éléments; et

Y est un groupe de liaison comprenant de l'azote, du phosphore, de l'oxygène ou du soufre, ou éventuellement Z et Y forment ensemble un système de cycles condensés.

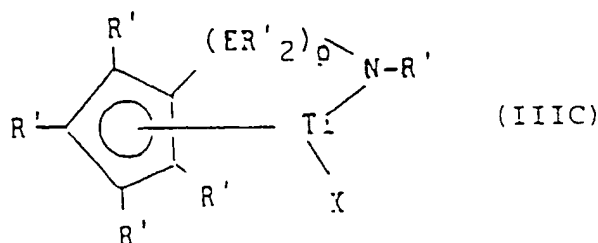
5. Procédé selon l'une des revendications précédentes, dans lequel ledit agent d'oxydation possède un potentiel d'oxydation d'au moins +0,20 volt.
6. Procédé selon l'une des revendications précédentes, dans lequel X_1, X_2, X_3 et X_4 sont des radicaux hydrocarbyle perfluorés contenant de 1 à 20 atomes de carbone.
7. Procédé selon la revendication 6, dans lequel ledit anion est un tétra(pentafluorophényl)borate.
8. Procédé selon l'une des revendications précédentes, dans lequel Ox^{+a} représente le ferrocénium, le ferrocénium substitué de façon inerte, ou Ag^{+1} .
9. Procédé selon l'une des revendications précédentes, dans lequel M représente le titane.
10. Procédé selon la revendication 4, dans lequel $L_f M^* X_n$ correspond à la formule IIIC



dans laquelle

R' dans chaque cas est choisi indépendamment parmi un atome d'hydrogène, un groupe silyle, alkyle aryle et leurs combinaisons ayant jusqu'à 10 atomes de carbone;
 E est un atome de silicium ou de carbone;
 X est un groupe hydrocarbyle ou un groupe hydrocarbyle substitué par un groupe alcoxy, amino, phosphino et/ou halogéno ayant jusqu'à 20 atomes de carbone; et
 p vaut 1 ou 2.

11. Procédé selon la revendication 10, dans lequel R' sur le groupe amido représente un groupe butyle.
12. Procédé selon la revendication 10, dans lequel E est un atome de silicium.
13. Procédé selon la revendication 10, dans lequel X est un groupe méthyle ou benzyle.
14. Procédé selon la revendication 4, dans lequel -Z-Y- est le (tert-butylamido)diméthylsilyle.
15. Procédé selon l'une des revendications précédentes, dans lequel le procédé est réalisé in situ au cours d'une réaction de polymérisation par addition en faisant passer ledit dérivé de métal réduit réactionnel et un agent oxydant dans le récipient de polymérisation.
16. Procédé selon l'une des revendications précédentes, consistant de plus à supporter le catalyseur sur un support.
17. Composé de formule IIIC



dans laquelle

R' dans chaque cas est choisi parmi un atome d'halogène, un groupe silyle, alkyle, aryle et leurs combinaisons ayant jusqu'à 10 atomes de carbone ou de silicium;
 E est un atome de silicium ou de carbone;
 X est un groupe hydrocarbyle ou un groupe hydrocarbyle substitué par un groupe alcoxy, amino, phosphino et halogéno ayant jusqu'à 20 atomes de carbone; et
 p vaut 1 ou 2.

18. Composé selon la revendication 17, dans lequel R' sur le groupe amido est un groupe butyle.
19. Composé selon la revendication 17, dans lequel E est un atome de silicium.

20. Composé selon la revendication 17, dans lequel X est un groupe méthyle ou benzyle.

21. Composé selon la revendication 17, choisi parmi le (tert-butylamido)diméthyl(tétraméthyl- η^5 -cyclopentadiényl)silane-
lanetane (III) (orthodiméthylamino)benzyle et le (tert-butylamido)diméthyl(tétraméthyl- η^5 -cyclopentadiényl)sila-
netane (III) allyle.

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